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(54) Certain 2-(2'-substituted benzoyl)-1,3-cyclohexanediones.

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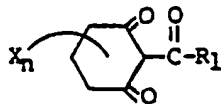
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**EP 0 186 119 B1**

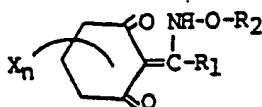
## EP 0 186 119 B1

## Description

Compounds having the structural formula



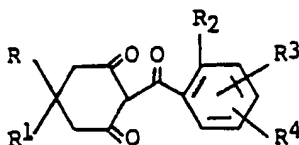
wherein X can be an alkyl, n can be 0, 1, or 2, and R<sub>1</sub> can be phenyl or substituted phenyl are described in Japanese Patent Application 84632-1974 as being intermediates for the preparation of herbicidal compounds of the formula



wherein R<sub>1</sub>, X, and n are as defined above and R<sub>2</sub> is alkyl, alkenyl, or alkynyl. Specifically taught herbicidal compounds of this latter group are those where n is 2, X is 5,5-dimethyl, R<sub>2</sub> is allyl and R<sub>1</sub> is phenyl, 4-chlorophenyl or 4-methoxyphenyl.

The precursor intermediates for these three specifically taught compounds have no or almost no herbicidal activity.

European Patent Application No. 83 102 599.4 was published October 5, 1983 and relates to certain novel 2-(2-substituted benzoyl)-cyclohexane-1,3-diones as herbicides. The compounds have the following structural formula



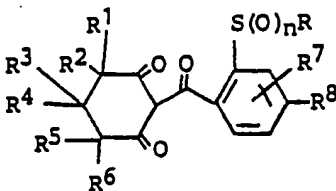
wherein R and R<sup>1</sup> are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>2</sup> is chlorine, bromine, or iodine; R<sup>3</sup> is hydrogen or halogen; and R<sup>4</sup> is hydrogen, chlorine, bromine, iodine, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, nitro or trifluoromethyl.

## Description of the Invention

This invention relates to 2-(2-benzoyl)-1,3-cyclohexanediones and their use as herbicides.

One embodiment of this invention is an herbicidal composition comprising an herbicidally active 2-(2-C<sub>1</sub>-C<sub>4</sub> alkylthio, C<sub>1</sub>-C<sub>4</sub> alkylsulfinyl or C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl benzyl)-1,3-cyclohexanedione and an inert carrier therefor. The 4-, 5- and 6-positions of the 1,3-cyclohexanedione moiety can be substituted, preferably with the groups hereinafter recited. More preferably, the 1,3-cyclohexanedione moiety has no substitution or the 4- or 6-positions are substituted with one or two methyl groups. The 3-, 4- and 5-positions of the benzoyl moiety can be substituted, preferably with the groups hereinafter recited.

Also embodied with the scope of this invention are novel compounds having the structural formula



wherein

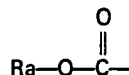
n is the integer 0, 1 or 2, preferably 2;

R is C<sub>1</sub>-C<sub>4</sub> alkyl, preferably methyl;

R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl, most preferably R<sup>1</sup> is hydrogen or methyl;

R<sup>2</sup> is hydrogen; C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl or

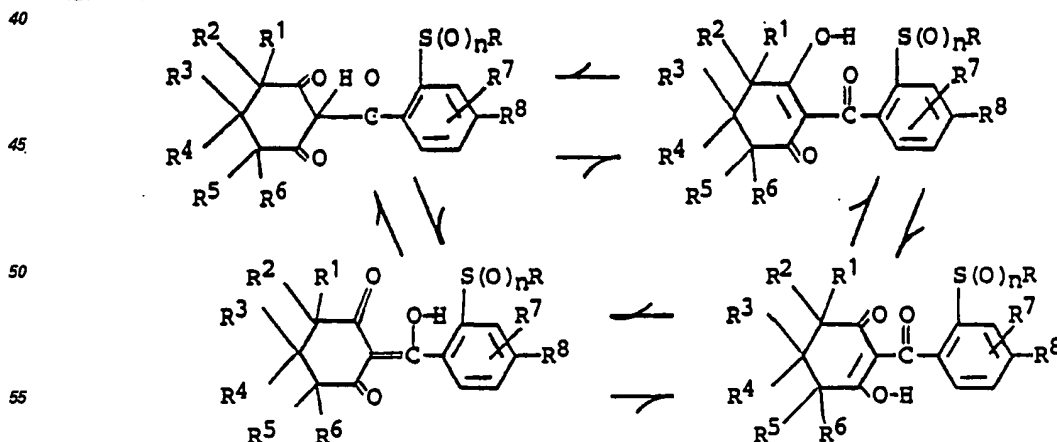
## EP 0 186 119 B1



- 5 wherein R<sup>a</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl, most preferably R<sup>a</sup> is hydrogen or methyl; or  
 R<sup>1</sup> and R<sup>2</sup> together are alkyl having 3 to 6 carbon atoms;  
 R<sup>3</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl, preferably C<sub>1</sub>—C<sub>2</sub> alkyl, more preferably methyl; most preferably R<sup>3</sup> is hydrogen or methyl;  
 R<sup>4</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl, preferably C<sub>1</sub>—C<sub>2</sub> alkyl, more preferably methyl; most preferably R<sup>4</sup> is hydrogen or methyl;  
 10 R<sup>5</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl, preferably C<sub>1</sub>—C<sub>2</sub> alkyl, more preferably methyl; most preferably R<sup>5</sup> is hydrogen or methyl;  
 R<sup>6</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl, preferably C<sub>1</sub>—C<sub>2</sub> alkyl, more preferably methyl, most preferably R<sup>6</sup> is hydrogen;  
 15 R<sup>7</sup> and R<sup>8</sup> independently are (1) hydrogen; (2) halogen, preferably chlorine, fluorine or bromine; (3) C<sub>1</sub>—C<sub>4</sub> alkyl, preferably methyl; (4) C<sub>1</sub>—C<sub>4</sub> alkoxy, preferably methoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>—C<sub>4</sub> haloalkyl, more preferably trifluoromethyl; (9) R<sup>b</sup>SO<sub>n</sub>— wherein n is the integer 0, 1 or 2, preferably 2; and  
 R<sup>b</sup> is (a) C<sub>1</sub>—C<sub>4</sub> alkyl, preferably methyl;  
 20 (b) C<sub>1</sub>—C<sub>4</sub> alkyl substituted with halogen or cyano, preferably chloromethyl, trifluoromethyl or cyanomethyl;  
 (c) phenyl; or  
 (d) benzyl;  
 (10) —NR<sup>c</sup>R<sup>d</sup> wherein  
 25 R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl;  
 (11) R<sup>c</sup>C(O)— wherein  
 R<sup>c</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl or C<sub>1</sub>—C<sub>4</sub> alkoxy; or  
 (12) —SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined, with the proviso that R<sup>7</sup> is not attached to the 6-position.  
 Preferably, R<sup>7</sup> is in the 3-position. Most preferably R<sup>7</sup> is hydrogen or 3-chlorine and R<sup>8</sup> is hydrogen, chlorine, fluorine, CF<sub>3</sub>, or R<sup>b</sup>SO<sub>2</sub> wherein R<sup>b</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl, preferably methyl.  
 30 The term "C<sub>1</sub>—C<sub>4</sub>" alkyl includes methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl and t-butyl. The term "halogen" includes chlorine, bromine, iodine and fluorine. The term "C<sub>1</sub>—C<sub>4</sub> alkoxy" includes methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy and t-butoxy. The term "haloalkyl" includes the eight alkyl groups with one or more hydrogens replaced by chloro, bromo, iodo or fluoro.  
 35 fluoro.

Salts of the above-described compounds (as defined hereinafter) are also the subject of the instant invention.

The compounds of this invention can have the following four structural formulae because of tautomerism:

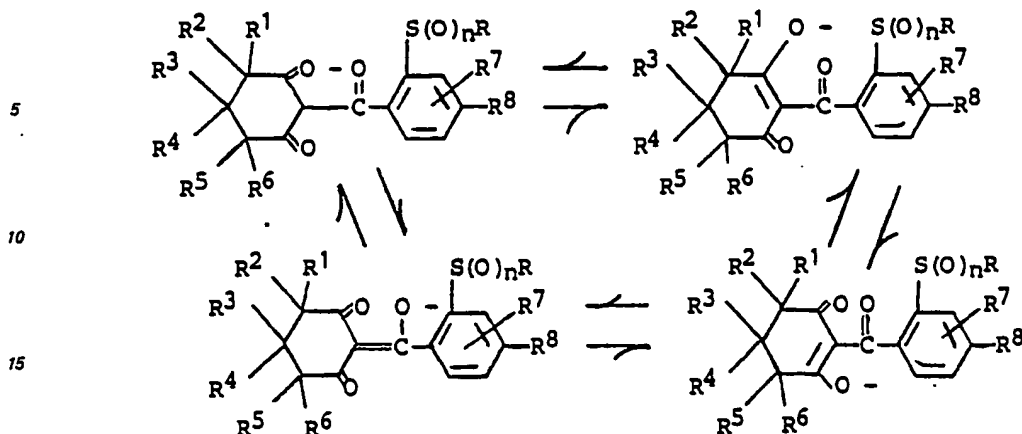


wherein n, R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are as defined above.

60 The circled proton on each of the four tautomers is reasonably labile. These protons are acidic and can be removed by any base to give a salt having an anion of the following four resonance forms:

65

## EP 0 186 119 B1



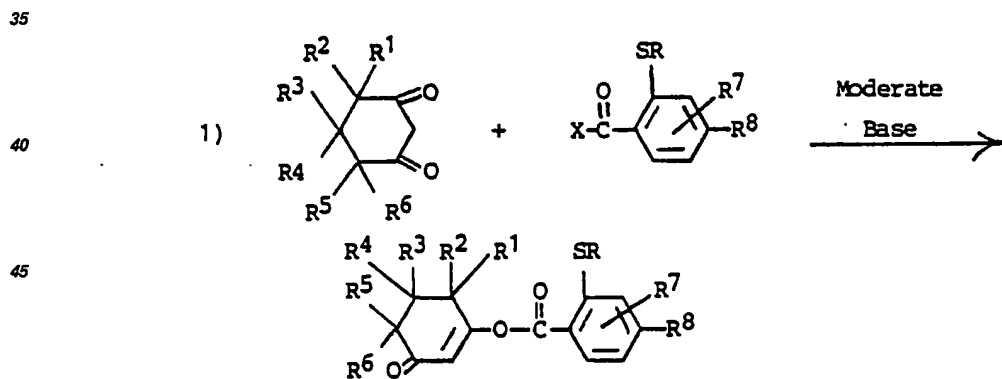
wherein  $n$ ,  $R$ ,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are as defined above.

Examples of cations of these bases are inorganic cations such as alkali metals e.g. lithium, sodium, and potassium organic cations such as substituted ammonium, sulfonium, or phosphonium wherein the substituent is an aliphatic or aromatic group.

The compounds of this invention and their salts are active herbicides of a general type. That is, they are herbicidally effective against a wide range of plant species. The method of controlling undesirable vegetation of the present invention comprises applying an herbicidally effective amount of the above-described compounds to the area where control is desired.

The compounds of the present invention can be prepared by the following two or three step general method.

The process proceeds via the production of an enol ester intermediate as shown in reaction (1). The final product is obtained by rearrangement of the enol ester as shown in reaction (2). The two reactions may be conducted as separate steps by isolation and recovery of the enol ester using conventional techniques prior to conducting step (2), or by addition of a cyanide source to the reaction medium after the formation of the enol ester, or in one step by inclusion of the cyanide source at the start of reaction (1).



wherein moderate base, and  $R$  through  $R^8$  are defined herein, and  $n$   $X$  is halogen, preferably chlorine,  $C_1-C_4$  alkyl- $C(O)-O-$ ,  $C_1-C_4$  alkoxy- $C(O)-O-$  or

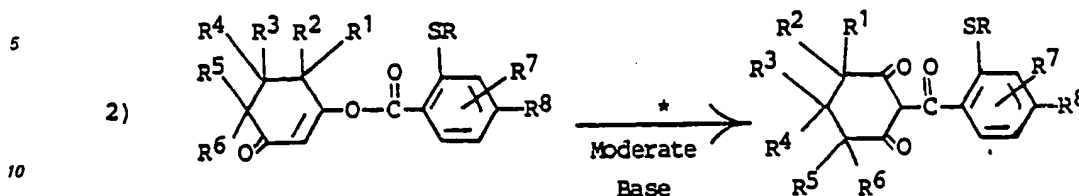


wherein  $R$ ,  $R^7$  and  $R^8$  in this portion of the molecule are identical with those in the reactant shown above, and the moderate base is as defined, preferably tri- $C_1-C_6$  alkylamine, pyridine, alkali metal carbonate or alkali metal phosphate.

Generally, in step (1) mole amounts of the dione and substituted benzoyl reactant are used, along with a mole amount or excess of the base. The two reactants are combined in an organic solvent such as methylene chloride, toluene, ethyl acetate or dimethylformamide. The base of benzoyl reactant preferably

## EP 0 186 119 B1

are added to the reaction mixture with cooling. The mixture is stirred at 0°C—50°C until the reaction is substantially complete.



\* = Cyanide source as defined herein. Moderate Base = As defined herein.

Generally, in step (2) a mole of the enol ester Intermediate is reacted with 1 to 4 moles of the base, preferably about 2 moles of moderate base and from 0.01 mole to about 0.5 mole or higher, preferably around 0.1 mole of the cyanide source (e.g. potassium cyanide or acetonecyano hydrin). The mixture is stirred in a reaction pot until the rearrangement is substantially complete at a temperature below 50°C, preferably about 20°C to about 40°C, and the desired product is recovered by conventional techniques.

The term "cyanide source" refers to a substance or substances which under the rearrangement conditions consists of or generates hydrogen cyanide and/or cyanide anion.

The process is conducted in the presence of a catalytic amount of a source of cyanide anion and/or hydrogen cyanide, together with a molar excess, with respect to the enol ester, of a moderate base.

Preferred cyanide sources are alkali metal cyanides such as sodium and potassium cyanide; cyanohydrins of methyl alkyl ketones having from 1—4 carbon atoms in the alkyl groups, such as acetone or methyl isobutyl ketone cyanohydrins; cyanohydrins of benzaldehyde or of C<sub>2</sub>—C<sub>5</sub> aliphatic aldehydes such as acetaldehyde, propionaldehyde, etc., cyanohydrins; zinc cyanide; tri(lower alkyl) silyl cyanides, notably trimethyl silyl cyanide; and hydrogen cyanide itself. Hydrogen cyanide is considered most advantageous as it produces relatively rapid reaction and is inexpensive. Among cyanohydrins the preferred cyanide source is acetone cyanohydrin.

The cyanide source is used in an amount up to about 50 mole percent based on the enol ester. It may be used in as little as about 1 mole percent to produce an acceptable rate of reaction at about 40°C on a small scale. Larger scale reactions give more reproducible results with slightly higher catalyst levels of about 2 mole percent. Generally about 1—10 mole % of the cyanide source is preferred.

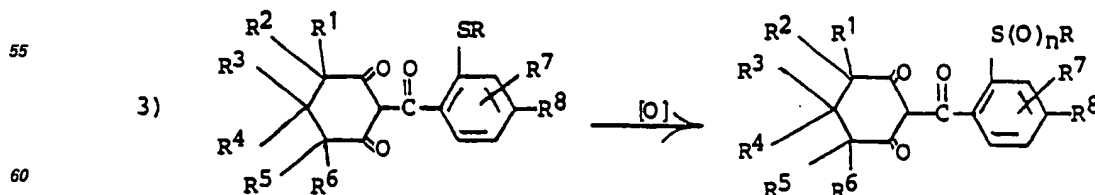
The process is conducted with a molar excess, with respect to the enol ester, of a moderate base. By the term "moderate base" is meant a substance which acts as a base yet whose strength or activity as a base lies between that of strong bases such as hydroxides (which could cause hydrolysis of the enol ester) and that of weak bases such as bicarbonates (which would not function effectively). Moderate bases suitable for use in this embodiment include both organic bases such as tertiary amines and inorganic bases such as alkali metal carbonates and phosphates. Suitable tertiary amines includes trialkylamines such as triethylamine, trialkanol-amines such as triethanolamine, and pyridine. Suitable inorganic bases include potassium carbonate and trisodium phosphate.

The base is used in an amount of from about 1 to 4 moles per mole of enol ester, preferably about 2 moles per mole.

When the cyanide source is an alkali metal cyanide, particularly potassium cyanide, a phase transfer catalyst may be included in the reaction. Particularly suitable phase transfer catalysts are the Crown ethers.

A number of different solvents may be useable in this process, depending on the nature of the acid chloride or the acrylated product. A preferred solvent for this reaction is 1,2-dichloroethane. Other solvents which may be employed, depending on the reactants or products include toluene, acetonitrile, methylene chloride, ethyl acetate, dimethylformamide, and methyl isobutyl ketone (MIBK).

In general, depending on the nature of the reactants and the cyanide source, the rearrangement may be conducted at temperatures up to about 50°C.



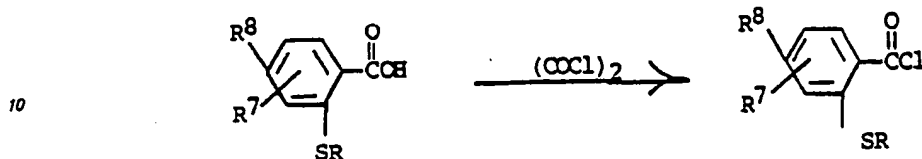
wherein n is 1 or 2.

Generally in step (3), a mole of the reaction product of step (2) is reacted with a slight mole or two mole excess of an oxidizing agent such as m-chloroperbenzoic acid after being dissolved in a solvent such as

## EP 0 186 119 B1

methylene chloride. After completion of the reaction, the resulting mixture is stripped under vacuum. The residue is purified by silica gel chromatography to yield the desired product.

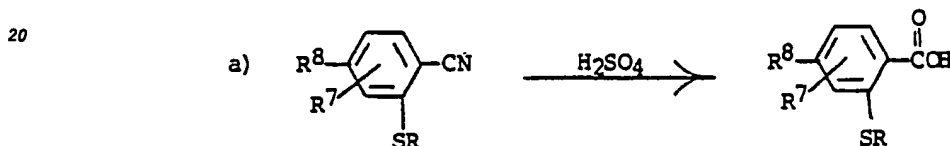
The above described substituted benzoyl chlorides can be prepared from the corresponding substituted benzoic acids according to the teaching of *Reagents for Organic Synthesis, Vol. I*, L. F. Fieser and M. Fieser, pp. 767—769 (1967).



wherein  $R$ ,  $R^7$  and  $R^8$  are as previously defined.

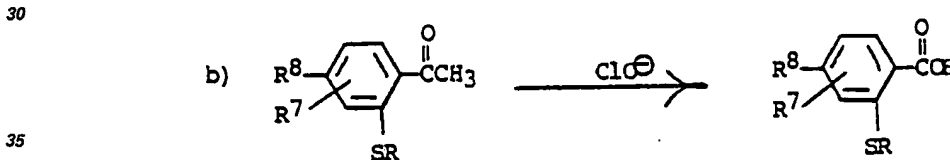
The substituted benzoic acids can be prepared by a wide variety of general methods according to the teaching of *The Chemistry of Carboxylic Acids and Esters*, S. Patai, editor, J. Wiley and Sons, New York, N.Y. (1969) and *Survey of Organic Synthesis*, C. A. Buehler and D. F. Pearson, J. Wiley and Sons, (1970).

The following are three representative examples of the methods described therein.



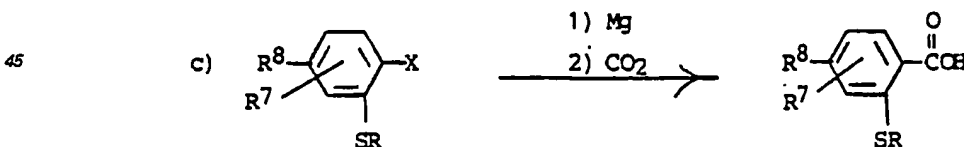
wherein  $R$ ,  $R^7$  and  $R^8$  are as previously defined.

In reaction (a) the substituted benzonitrile is heated to reflux in aqueous sulfuric acid for several hours. The mixture is cooled and the reaction product is isolated by conventional techniques.



wherein  $R$ ,  $R^7$  and  $R^8$  are as previously defined.

In reaction (b) the substituted acetophenone is heated to reflux for several hours in an aqueous hypochlorite solution. The mixture is cooled and the reaction product is isolated by conventional techniques.



wherein  $R$ ,  $R^7$  and  $R^8$  are as defined and  $X$  is chlorine, bromine or iodine.

In reaction (c) the substituted aromatic halide is allowed to react with magnesium in a solvent such as ether. The solution is then poured over crushed dry ice and the benzoic acid is isolated by conventional techniques.

The following examples teach the synthesis representative compounds of this invention.

## Example 1

2-(2'-Methylthiobenzoyl)-4,4,6-trimethyl-1,3-cyclohexanedione



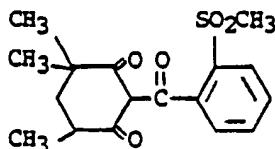
2-Methylthiobenzoyl chloride (7.2 g, 39 mmol) and 4,4,6-trimethylcyanoheptanedione (5.0 g, 39 mmol)

## EP 0 186 119 B1

were dissolved in methylene chloride. Triethylamine (7.0 ml, 50 mmol) was added dropwise and the resulting solution stirred for one hour at room temperature. The solution was washed with 2 normal hydrochloric acid (2N HCl), 5% potassium carbonate solution (5% K<sub>2</sub>CO<sub>3</sub>) and saturated sodium chloride solution (brine), dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>) and concentrated under vacuum. The residue was dissolved in 20 ml acetonitrile. Triethylamine (2.5 equivalents) and acetone cyanohydrin (0.4 ml) were added and the solution stirred for 45 minutes at room temperature. After dilution with ether, the solution was washed with 2N HCl and extracted with 5% K<sub>2</sub>CO<sub>3</sub>. The aqueous extract was acidified with hydrochloric acid and extracted with ether. The ether was washed with brine, dried (MgSO<sub>4</sub>) and concentrated under vacuum. The residue was purified by trituration with ether, yielding 5.0 g of a viscous oil which was identified as the desired compound by nuclear magnetic resonance spectroscopy (nmr), infrared spectroscopy (ir) and mass spectroscopy (ms).

## Example 2

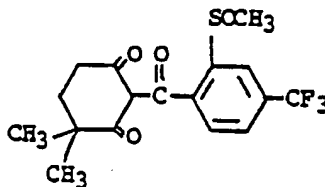
2-(2'-Methanesulfonylbenzoyl)-4,4,6-trimethyl-1,3-cyclohexanedione



The benzoyl cyclohexanedione prepared in Example 1 (2.5 g, 7.9 mmol) was dissolved in 40 ml methylene chloride. M-Chloroperbenzoic acid (3.5 g, 16 mol) was added and the resulting solution was stirred for 45 minutes. The solution was concentrated under vacuum. Purification of the residue by silica gel chromatography yielded 1.7 g of a viscous oil which was identified as the desired compound by nmr, ir and ms.

## Example 3

2-(4'-Trifluoromethyl-2'-methanesulfinylbenzoyl)-4,4-dimethyl-1,3-cyclohexanedione



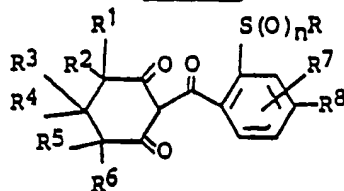
2-(4'-Trifluoromethyl-2'-methylthiobenzoyl)-4,4-dimethyl-1,3-cyclohexanedione (5.0 g, 14 mmol) (which was prepared according to the method of Example 1) was dissolved in 50 ml methylene chloride. A solution of m-chloroperbenzoic acid (2.4 g—80%, 14 mmol) in 50 ml methylene chloride was added dropwise and the resulting solution was stirred for three hours at room temperature. After concentration under vacuum, the residue was dissolved in ether and washed with 1% hydrochloric acid. A 5% copper(II) acetate solution was added to the ether fraction, followed by hexane. The liquid phase was decanted and the remaining gummy solid stirred with 6N HCl and ether. The ether layer was dried (MgSO<sub>4</sub>) and concentrated to give 4.7 g of a thick yellow solid. Purification on a centrifugally accelerated thin layer chromatograph (4 mm silica gel, 50:50:1 hexane:ethyl acetate:acetic acid — eluent) yielded 2.4 g of a viscous oil which was identified as the desired compound by nmr, ir and ms.

The following is a table of certain selected compounds that are prepared according to the procedure described hereto. Compound numbers are assigned to each compound and are used throughout the remainder of the application.



## EP 0 186 119 B1

TABLE I



Comp. No.	n	R	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	R <sup>8</sup>	m.p.
1	0	CH <sub>3</sub>	H	H	H	H	H	H	H	H	79-81°C
2	0	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	H	oil
3a)	0	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	H	oil
4b)	2	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	H	oil
5	0	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	H	oil
6	2	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	H	oil
7	0	CH <sub>3</sub>	H	H	H	H	H	H	3-Cl	Cl	59-64°C
8	2	CH <sub>3</sub>	H	H	H	H	H	H	3-Cl	Cl	116-119°C
9	0	CH <sub>3</sub>	H	H	H	H	H	H	H	CF <sub>3</sub>	102-106°C
10	2	CH <sub>3</sub>	H	H	H	H	H	H	H	CF <sub>3</sub>	oil
11	0	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CF <sub>3</sub>	49-53°C
12	2	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CF <sub>3</sub>	oil
13c)	1	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CF <sub>3</sub>	oil
14	0	CH <sub>3</sub>	H	H	H	H	H	H	3-Cl	-SCH <sub>3</sub>	105-107°C
15	1	CH <sub>3</sub>	H	H	H	H	H	H	3-Cl	-S(O)CH <sub>3</sub>	oil
16	0	CH <sub>3</sub>	H	H	H	H	H	H	H	-SO <sub>2</sub> n-C <sub>3</sub> H <sub>7</sub>	oil
17	0	CH <sub>3</sub>	H	H	H	H	H	H	H	-SCH <sub>3</sub>	101-103°C
18	2	CH <sub>3</sub>	H	H	H	H	H	H	H	-SO <sub>2</sub> n-C <sub>3</sub> H <sub>7</sub>	oil
19	2	CH <sub>3</sub>	H	H	H	H	H	H	H	-SO <sub>2</sub> CH <sub>3</sub>	194-196°C
20	0	CH <sub>3</sub>	H	H	H	H	H	H	3-CH <sub>3</sub>	H	40-42°C
21	2	CH <sub>3</sub>	H	H	H	H	H	H	3-CH <sub>3</sub>	H	80-86°C

a) Prepared in Example 1.

b) Prepared in Example 2.

c) Prepared in Example 3.

## Herbicidal Screening Tests

As previously mentioned, the herein described compounds produced in the above-described manner are phytotoxic compounds which are useful and valuable in controlling various plant species. Selected compounds of this invention were tested as herbicides in the following manner.

**Pre-emergence herbicide test.** On the day preceding treatment, seeds of eight different weed species are planted in loamy sand soil in individual rows using one species per row across the width of a flat. The seeds used are green foxtail (FT) (*Setaria viridis*), watergrass (WG) (*Echinochloa crusgalli*), wild oat (WO) (*Avena fatua*), annual morning-glory (AMG) (*Ipomoea lacunosa*), velvetleaf (VL) (*Abutilon theophrasti*), Indian mustard (MD) (*Brassica juncea*), curly dock (CD) (*Rumex crispus*), and yellow nutsedge (YNG) (*Cyperus esculentus*). Ample seeds are planted to give about 20 to 40 seedlings per row, after emergence, depending upon the size of the plants.

Using an analytical balance, 600 milligrams (mg) of the compound to be tested are weighed out on a piece of glassine weighing paper. The paper and compound are placed in a 60 milliliter (ml) wide-mouth

**EP 0 186 119 B1**

clear bottle and dissolved in 45 ml of acetone or substituted solvent. Eighteen ml of this solution are transferred to a 60 ml wide-mouth clear bottle and diluted with 22 ml of a water and acetone mixture (19:1) containing enough polyoxyethylene sorbitan monolaurate emulsifier to give a final solution of 0.5% (v/v). The solution is then sprayed on a seeded flat on a linear spray table calibrated to deliver 80 gallons per acre (748 L/ha). The application rate is 4 lb/acre (4.48 Kg/ha).

After treatment, the flats are placed in the greenhouse at a temperature of 70 to 80°F and watered by sprinkling. Two weeks after treatment, the degree of injury or control is determined by comparison with untreated check plants of the same age. The injury rating from 0 to 100% is recorded for each species as percent control with 0% representing no injury and 100% representing complete control.

The results of the tests are shown in the following Table II.

**TABLE II**  
Pre-Emergence Herbicidal Activity  
Application Rate — 4.48 kg/ha

Cmpd. No.	FT	WG	WO	AMG	VL	MD	CD	YNG
1	0	0	0	0	0	0	0	20
2	25	30	30	0	70	0	40	30
3	25	20	0	0	0	0	0	0
4	100	100	90	60	100	100	100	90
5	50	60	40	50	50	60	90	50
6	100	95	50	40	40	60	99	70
16	80	100	50	60	100	90	90	90
20	100	100	30	15	100	100	90	85
21	100	100	-	30	100	95	100	80

A blank (-) indicates that the weed was not tested.

*Post-Emergence Herbicide Test:* This test is conducted in an identical manner to the testing procedure for the pre-emergence herbicide test, except the seeds of the eight different weed species are planted 10—12 days before treatment. Also, watering of the treated flats is confined to the soil surface and not to the foliage of the sprouted plants.

The results of the post-emergence herbicide test are reported in Table III.

**TABLE III**  
Post-Emergence Herbicidal Activity  
Application Rate — 4.48 kg/ha

Cmpd. No.	FT	WG	WO	AMG	VL	MD	CD	YNG
1	20	20	10	20	40	40	20	40
2	0	60	60	50	70	30	0	15
3	20	20	0	10	0	20	0	20
4	85	90	100	45	75	30	80	65
5	55	50	60	50	75	85	65	-
6	70	70	50	60	80	70	90	-
16	95	95	40	100	100	100	100	90
20	95	75	35	40	95	75	35	80
21	80	70	30	45	80	90	50	70

A blank (-) indicates the weed was not tested.

*Pre-Emergence Multi-Weed Herbicide Test:* Several compounds were evaluated at an application rate of 2 or 1 lb/acre (2.24 or 1.12 kg/ha) for preemergence activity against a larger number of weed species.

The process was generally similar to the pre-emergence herbicide test described above except that only 300, 150 or 37.5 milligrams of test compound were weighed out and the application rate was 40 gallons per acre.

**EP 0 186 119 B1**

Redroot pigweed (PW) and curly dock (CD) were eliminated in this test and the following weed species were added:

5	Grasses:	downy brome	<i>Bromus tectorum</i>	(DB)
		annual ryegrass	<i>Lolium multiflorum</i>	(ARG)
		Johnsongrass	<i>Sorghum halepense</i>	(JG)
		broadleaf signalgrass	<i>Brachiaria platyphylla</i>	(BSG)
		hemp sesbania	<i>Sesbania exaltata</i>	(SESB)
10		sicklepod	<i>Cassia obtusifolia</i>	(SP)

The results of the test are shown in Tables IV and V.

**TABLE IV****Pre-Emergence Multi-weed Herbicide Test**

Application Rate - 2.24 kg/ha

15	Ompd.													
20	No.	DB	FT	ARG	WG	JG	WO	BSG	AMG	SESB	VL	SP	MD	YNG
	17	95	85	35	100	85	25	90	100	100	100	40	100	95
	18	0	0	0	50	20	0	15	60	45	100	0	100	-

**TABLE V****Pre-Emergence Multi-weed Herbicide Test**

Application Rate - 1.12 kg/ha

25	Ompd.													
30	No.	DB	FT	ARG	WG	JG	WO	BSG	AMG	SESB	VL	SP	MD	YNG
	7	30	70	20	100	75	0	90	100	95	100	100	100	90
	8	95	95	45	100	98	25	90	100	95	100	90	100	90
35	9	10	70	40	100	20	0	80	100	85	100	40	100	95
	10	100	100	10	100	40	0	90	100	100	100	80	100	100
	11	90	100	90	100	100	65	100	100	90	100	30	100	65
	12	100	100	80	100	100	85	90	100	100	100	85	100	90
40	13	0	100	10	100	100	80	70	80	90	100	70	100	80
	15	0	10	0	90	0	0	15	35	30	100	10	85	75
	19	100	90	0	100	20	10	40	95	100	100	100	100	65

**Post-Emergence Multi-Weed Herbicide Test:** This test is conducted in an identical manner to the testing procedure for the postemergence herbicide test, except the seeds of the eight weed species used in the pre-emergence multi-weed herbicide test were used and the seeds were planted 10—12 days before treatment. Also, watering of the treated flats is confined to the soil surface and not to the foliage of the sprouted plants.

The results of the post-emergence multi-weed herbicide test are reported in Tables VI and VII.

**TABLE VI****Post-Emergence Multi-Weed Herbicidal Activity**

Application Rate - 2.24 kg/ha

55	Ompd.													
60	No.	DB	FT	ARG	WG	JG	WO	BSG	AMG	SESB	VL	SP	MD	YNG
	17	80	100	55	95	90	20	60	100	100	100	75	100	70
	18	0	100	0	98	20	0	10	70	60	100	10	100	45

## EP 0 186 119 B1

TABLE VII

Post-Emergence Multi-Weed Herbicidal Activity  
Application Rate — 1.12 kg/ha

5	Cmpd.		FT	ARG	WG	JG	WO	BSG	AMG	SESB	VL	SP	MD	YNG
	No.	DB												
	7	25	30	0	70	60	20	90	75	95	85	50	100	35
	8	80	80	20	70	70	40	80	50	80	80	60	60	35
10	9	0	30	0	75	15	25	100	95	100	100	60	100	25
	10	60	80	20	70	35	25	80	75	90	90	70	100	45
	11	45	100	20	100	100	40	50	100	100	100	20	100	35
	12	70	60	30	100	100	80	98	90	100	100	70	98	40
15	13	25	100	10	100	100	85	100	80	100	100	10	90	25
	15	30	65	10	90	50	30	20	85	80	98	30	65	15
	19	20	60	10	90	10	15	90	100	100	70	100	40	85

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The compounds of the present invention are useful as herbicides and can be applied in a variety of ways at various concentrations. In practice, the compounds herein defined are formulated into herbicidal compositions, by admixture, in herbicidally effective amounts, with the adjuvants and carriers normally employed for facilitating the dispersion of active ingredients for agricultural applications, recognizing the fact that the formulation and mode of application of a toxicant may affect the activity of the materials in a given application. Thus, these active herbicidal compounds may be formulated as granules of relatively large particle size, as wettable powders, as emulsifiable concentrates, as solutions or as any of several other known types of formulations, depending upon the desired mode of other known types of formulations, depending upon the desired mode of application. Preferred formulations for pre-emergence herbicidal applications are wettable powders, emulsifiable concentrates and granules. These formulations may contain as little as about 0.5% to as much as about 95% or more by weight of active ingredient. A herbicidally effective amount depends upon the nature of the seeds or plants to be controlled and the rate of application varies from about 0.05 to approximately 25 pounds per acre, preferably from about 0.1 to about 10 pounds per acre.

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Wettable powders are in the form of finely divided particles which disperse readily in water or other dispersants. The wettable powder is ultimately applied to the soil either as a dry dust or as a dispersion in water or other liquid. Typical carriers for wettable powders include fuller's earth, kaolin clays, silicas and other readily wet organic or inorganic diluents. Wettable powders normally are prepared to contain about 5% to about 95% of the active ingredient and usually also contain a small amount of wetting, dispersing, or emulsifying agent to facilitate wetting and dispersion.

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Emulsifiable concentrates are homogeneous liquid compositions which are dispersed in water or other dispersant, and may consist entirely of the active compound with a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthal, isophorone and other non-volatile organic solvents. For herbicidal application, these concentrates are dispersed in water or other liquid carrier and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises about 0.5 to 95% of active ingredient by weight of the herbicidal composition.

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Granular formulations wherein the toxicant is carried on relatively coarse particles, are usually applied without dilution to the area in which suppression of vegetation is desired. Typical carriers for granular formulations include sand, fuller's earth, bentonite clays, vermiculite, perlite and other organic or inorganic materials which absorb or which may be coated with the toxicant. Granular formulations normally are prepared to contain about 5% to about 25% of active ingredients which may include surface-active agents such heavy aromatic naphthas, kerosene or other petroleum fractions, or vegetable oils; and/or stickers such as destrins, glue or synthetic resins.

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Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, for example, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; polyhydric alcohols; and other types of surface-active agents, many of which are available in commerce. The surface-active agent, when used, normally comprises from 0.1% to 15% by weight of the herbicidal composition.

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Dusts, which are free-flowing admixtures of the active ingredient with finely divided solids such as talc, clays, flours and other organic and inorganic solids which act as dispersants and carriers for the toxicant, are useful formulations for soil-incorporating application.

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Pastes, which are homogeneous suspensions of a finely divided solid toxic in a liquid carrier such as water or oil, are employed for specific purposes. These formulations normally contain about 5% to about 95% of active ingredient by weight, and may also contain small amounts of a wetting dispersing or emulsifying agent to facilitate dispersion. For application, the pastes are normally diluted and applied and

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**EP 0 186 119 B1**

applied as a spray to the area to be affected.

Other useful formulations for herbicidal applications include simple solutions of the active ingredient in a dispersant in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene and other organic solvents. Pressurized sprays, typically aerosols, wherein the active ingredient is dispersed in finely-divided form as a result of vaporization of a low boiling dispersion solvent carrier, such as the Freons, may also be used.

The phytotoxic compositions of this invention are applied to the plants in the conventional manner. Thus, the dust and liquid compositions can be applied to the plant by the use of power-dusters, boom and hand sprayers and spray dusters. The compositions can also be applied from airplanes as a dust or a spray because they are effective in very low dosages. In order to modify or control growth of germinating seeds or emerging seedlings, as a typical example, the dust and liquid compositions are applied to the soil according to conventional methods and are distributed in the soil to a depth of at least  $\frac{1}{2}$  inch below the soil surface. It is not necessary that the phytotoxic compositions be admixed with the soil particles since these compositions can also be applied merely by spraying or sprinkling the surface of the soil. The phytotoxic compositions of this invention can also be applied by addition to irrigation water supplied to the field to be treated. This method of application permits the penetration of the compositions into the soil as the water is absorbed therein. Dust compositions, granular compositions or liquid formulations applied to the surface of the soil can be distributed below the surface of the soil by conventional means such as discing, dragging or mixing operations.

**EMULSIFIABLE CONCENTRATE FORMULATIONS**

<i>General Formula with Ranges</i>		<i>Specific Formula</i>	
herbicidal compound	5—55	herbicidal compound	54
surfactant(s)	5—25	proprietary blend of oil-soluble sulfonates and polyoxyethylene ethers	10
solvent(s)	20—90	polar solvent	27
	100%	petroleum hydrocarbon	9
			100%

**WETTABLE POWDER FORMULATIONS**

herbicidal compound	3—90	herbicidal compound	80
wetting agent	0.5—2	sodium dialkyl naphthalene sulfonate	0.5
dispersing agent	1—8	sodium lignosulfonate	7
diluent(s)	8.5—87	attapulgate clay	12.5
	100%		100%

**EXTRUDED GRANULAR FORMULATIONS**

herbicidal compound	1—20	herbicidal compound	10
binding agent	0—10	lignin sulfonate	5
diluent(s)	70—99	calcium carbonate	85
	100%		100%

**FLOWABLE FORMULATIONS**

herbicidal compound	20—70	herbicidal compound	45
surfactant(s)	1—10	polyoxyethylene ether	5
suspending agent(s)	0.05—1	attagel	0.05
antifreeze agent	1—10	propylene glycol	10
antimicrobial agent	1—10	BIT	0.03
antifoam agent	0.1—1	silicone defoamer	0.02
solvent	7.95—77.85	water	39.9
	100%		100%

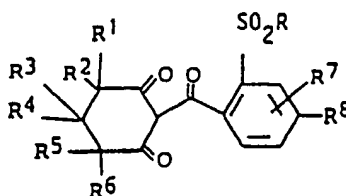
The phytotoxic compositions of this invention can also contain other additives, for example, fertilizers and other herbicides, pesticides and the like, used as adjuvant or in combination with any of the above-described adjuvants. Other phytotoxic compounds useful in combination with the above-described

## EP 0 186 119 B1

compounds include, for example, anilides such as 2-benzothiazole-2-yloxy-N-methyl acetanilide, 2-chloro-2',6'-dimethyl-N-(n-propylethyl) acetanilide, 2-chloro-2',6'-diethyl-N-(butoxymethyl) acetanilide; 2,4-dichlorophenoxyacetic acids, 2,4,5-trichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid and the salts, esters and amides thereof; triazine derivatives, such as 2,4-bis(3-methoxypropylamino)-6-methylthio-s-triazine, 2-chloro-4-ethylamino-6-isopropylamino-s-triazine, and 2-ethylamino-4-isopropyl-amino-6-methyl-mercapto-s-triazine; urea derivatives, such as 3-(3,5-dichlorophenyl)-1,1-dimethylurea and 3-(p-chlorophenyl)-1,1-dimethylurea; and acetamides such as N,N-diallyl- $\alpha$ -chloroacetamide, and the like; benzoic acids such as 3-amino-2,5-dichlorobenzoic acid; thiocarbamates such as S-(1,1-dimethylbenzyl)-piperidine-1-carbothioate, 3-(4-chlorophenyl)-methyl diethylcarbothioate, ethyl-1-hexahydro-1,4-azepine-1-carbothioate, S-ethyl-hexahydro-1H-azepine-1-carbothioate, S-propyl N,N-dipropylthiocarbamate, S-propyl N,N-di-n-propylthiocarbamate, S-ethyl cyclohexylethylthiocarbamate and the like; anilines such as 4-(methylsulfonyl)-2,6-dinitro-N,N substituted aniline, 4-trifluoromethyl-2,6-dinitro-N,N-di-n-propyl aniline, 4-trifluoromethyl-2,6-dinitro-N-ethyl-N-butyl aniline, 2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid, 2-[1-(ethoxyimino)butyl]-5-[2-ethylthio]propyl]-3-hydroxy-2-cyclohexene-1-one, ( $\pm$ )-butyl-2-[4-[(5-trifluoromethyl)-2-pyridinyl]oxy]-phenoxy]propanate, sodium 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-fluoromethyl]phenoxy]-2-nitrobenzoate, 3-isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one-2,2-dioxide, and 4-amino-6-tert-butyl-3-(methylthio)-astriazin-5(4H)-one or 4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one and S-(O,O-diisopropyl)-benzene sulfonamide. Fertilizers useful in combination with the active ingredient include, for example, ammonium nitrate, urea and superphosphate. Other useful additaments include materials in which plant organisms take root and grow such as compost, manure, humus, sand, and the like.

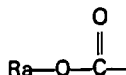
## Claims

1. A compound of the formula



wherein

R is C<sub>1</sub>—C<sub>4</sub> alkyl;  
R<sup>1</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl;  
R<sup>2</sup> is hydrogen; C<sub>1</sub>—C<sub>4</sub> alkyl, or



wherein R<sup>a</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl; or

R<sup>1</sup> and R<sup>2</sup> together are alkylene having 3 to 6 carbon atoms;  
R<sup>3</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl;  
R<sup>4</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl;  
R<sup>5</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl;  
R<sup>6</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl; and  
R<sup>7</sup> and R<sup>8</sup> independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>—C<sub>4</sub> alkyl; (4) C<sub>1</sub>—C<sub>4</sub> alkoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>—C<sub>4</sub> haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>— wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>—C<sub>4</sub> alkyl; (b) C<sub>1</sub>—C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10) —NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl; (11) R<sup>c</sup>C(O)— wherein R<sup>c</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl or C<sub>1</sub>—C<sub>4</sub> alkoxy; or (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined, with the proviso that R<sup>7</sup> is not attached to the 6-position.

2. The compounds of Claim 1 wherein R is methyl; R<sup>1</sup> is hydrogen or methyl; R<sup>2</sup> is hydrogen or methyl; R<sup>3</sup> is hydrogen or methyl; R<sup>4</sup> is hydrogen or methyl; R<sup>5</sup> is hydrogen or methyl; R<sup>6</sup> is hydrogen or methyl; R<sup>7</sup> and R<sup>8</sup> independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>—C<sub>4</sub> alkyl; (4) C<sub>1</sub>—C<sub>4</sub> alkoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>—C<sub>4</sub> haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>— wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>—C<sub>4</sub> alkyl; (b) C<sub>1</sub>—C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10) —NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl; (11) R<sup>c</sup>C(O)— wherein R<sup>c</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl or C<sub>1</sub>—C<sub>4</sub> alkoxy; or (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined.

3. The compound of claim 2 wherein R<sup>7</sup> and R<sup>8</sup> are independently are hydrogen; chlorine; fluorine; bromine; methyl; methoxy; OCF<sub>3</sub>; cyano; nitro; trifluoromethyl; R<sup>b</sup>SO<sub>n</sub>— wherein n is the integer 2 and R<sup>b</sup> is methyl, chloromethyl, trifluoromethyl, cyanomethyl, ethyl, or n-propyl; —NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl; R<sup>c</sup>C(O)— where R<sup>c</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl or C<sub>1</sub>—C<sub>4</sub> alkoxy or SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined and R<sup>7</sup> is in the 3-position.

4. The compounds of Claim 2 wherein R<sup>7</sup> is hydrogen and R<sup>8</sup> is hydrogen, chlorine, bromine, fluorine,

## EP 0 186 119 B1

CF<sub>3</sub> or R<sup>b</sup>SO<sub>2</sub> wherein R<sup>b</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl.

5. The compounds of Claim 2 wherein R is methyl; R<sup>1</sup> is methyl; R<sup>2</sup> is methyl; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is hydrogen; R<sup>6</sup> is hydrogen; R<sup>7</sup> is hydrogen; and R<sup>8</sup> is hydrogen.

6. The compounds of Claim 2 wherein R is methyl; R<sup>1</sup> is methyl; R<sup>2</sup> is methyl; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is methyl; R<sup>6</sup> is hydrogen; R<sup>7</sup> is hydrogen; and R<sup>8</sup> is hydrogen.

7. The compounds of Claim 2 wherein R is methyl; R<sup>1</sup> is hydrogen; R<sup>2</sup> is hydrogen; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is hydrogen; R<sup>6</sup> is hydrogen; R<sup>7</sup> is 3-chlorine; and R<sup>8</sup> is chlorine.

8. The compound of Claim 2 wherein R is methyl; R<sup>1</sup> is hydrogen; R<sup>2</sup> is hydrogen; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is hydrogen; R<sup>6</sup> is hydrogen; R<sup>7</sup> is hydrogen; and R<sup>8</sup> is trifluoromethyl.

9. The compounds of Claim 2 wherein R is methyl; R<sup>1</sup> is methyl; R<sup>2</sup> is methyl; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is hydrogen; R<sup>6</sup> is hydrogen; R<sup>7</sup> is hydrogen; and R<sup>8</sup> is trifluoromethyl.

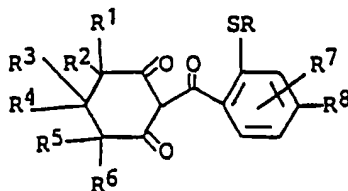
10. The method of controlling undesirable vegetation comprising applying to the area when control is desired, and herbicidally effective amount of a compound of claims 1—9.

11. An herbicidal composition comprising an herbicidally active 2-(2-C<sub>1</sub>—C<sub>4</sub> alkylthio, C<sub>1</sub>—C<sub>4</sub> alkylsulfinyl or C<sub>1</sub>—C<sub>4</sub> alkylsulfonyl benzoyl)-1,3-cyclohexanedione and an inert carrier therefor.

12. The herbicidal composition of Claim 11 wherein the 2-(2-C<sub>1</sub>—C<sub>4</sub> alkylthio, C<sub>1</sub>—C<sub>4</sub> alkylsulfinyl or C<sub>1</sub>—C<sub>4</sub> alkylsulfonyl benzoyl)-1,3-cyclohexanedione is a compound of Claims 1—9.

13. A process for preparing a compound of the formula

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wherein

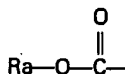
R is C<sub>1</sub>—C<sub>4</sub> alkyl;

30 R is C<sub>1</sub>—C<sub>4</sub> alkyl, optionally substituted with halogen;

R<sup>1</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl;

R<sup>2</sup> is hydrogen; C<sub>1</sub>—C<sub>4</sub> alkyl, or

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wherein R<sup>a</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl; or

R<sup>1</sup> and R<sup>2</sup> together are alkylene having 3 to 6 carbon atoms;

R<sup>3</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl;

40 R<sup>4</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl;

R<sup>5</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl;

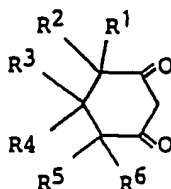
R<sup>6</sup> is hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl; and

R<sup>7</sup> and R<sup>8</sup> independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>—C<sub>4</sub> alkyl; (4) C<sub>1</sub>—C<sub>4</sub> alkoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>—C<sub>4</sub> haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>— wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>—C<sub>4</sub> alkyl; (b) C<sub>1</sub>—C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10) —NR<sup>e</sup>R<sup>d</sup> wherein R<sup>e</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>—C<sub>4</sub> alkyl; (11) R<sup>c</sup>C(O)— wherein R<sup>c</sup> is C<sub>1</sub>—C<sub>4</sub> alkyl or C<sub>1</sub>—C<sub>4</sub> alkoxy; or (12) SO<sub>2</sub>NR<sup>e</sup>R<sup>d</sup> wherein R<sup>e</sup> and R<sup>d</sup> are as defined, with the proviso that R<sup>7</sup> is not attached to the 6-position comprising

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(a) reacting a dione of the formula

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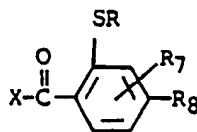


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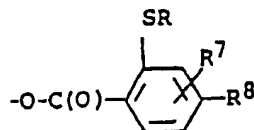
60 wherein R<sup>1</sup> through R<sup>6</sup> are as defined with a substituted benzoyl reactant of the formula

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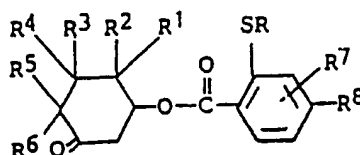
## EP 0 186 119 B1



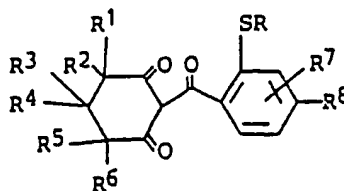
wherein R, R<sup>7</sup> and R<sup>8</sup> are as defined and X is halogen, C<sub>1</sub>—C<sub>4</sub>alkyl-C(O)—O—, C<sub>1</sub>—C<sub>4</sub> alkoxy-C(O)—O— or



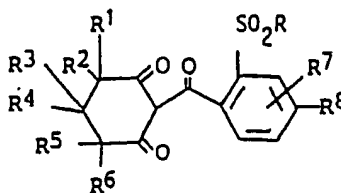
wherein R, R<sup>7</sup> and R<sup>8</sup> in this portion of the molecule are identical with those in the reactant shown above with at least a mole of a moderate base to form an enol ester of the formula



wherein R through R<sup>8</sup> are as defined and in step (2) reacting a mole of the enol ester intermediate with 1 to 4 moles of a moderate base, and from 0.01 mole to about 0.5 mole or higher of a cyanide source to form a 2—C<sub>1</sub>—C<sub>4</sub> alkylthiobenzoyl compound of the formula



wherein R<sup>1</sup> through R<sup>8</sup> are as defined above and optionally oxidizing the 2—C<sub>1</sub>—C<sub>4</sub> alkylthiobenzoyl compound with a mole or two moles of an oxidizing agent to form a compound of the formula



where R through R<sup>8</sup> are as defined.

14. The process of Claim 13 wherein X is halogen, the moderate base is tri-C<sub>1</sub>—C<sub>6</sub> alkylamine, pyridine, alkali metal carbonate or alkali metal phosphate and the cyanide source alkali metal cyanide, cyanohydrins of methyl C<sub>1</sub>—C<sub>4</sub> alkyl ketones, cyanohydrins of benzaldehyde or C<sub>2</sub>—C<sub>5</sub> aliphatic aldehydes; cyanohydrins, zinc cyanide; tri(lower alkyl) silyl cyanides or hydrogen cyanide.

15. The process of Claim 14 wherein X is chlorine, the moderate base is tri-C<sub>1</sub>—C<sub>6</sub> alkylamine, pyridine, sodium carbonate or sodium phosphate and the cyanide source is potassium cyanide, acetone cyanohydrin or hydrogen cyanide.



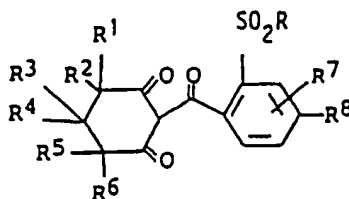
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## Patentansprüche

## 1. Verbindung der Formel

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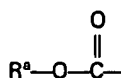


worin

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R C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet,  
 R<sup>1</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet,  
 R<sup>2</sup> Wasserstoff, C<sub>1</sub>—C<sub>4</sub>-Alkyl oder

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bedeutet, worin R<sup>a</sup> für C<sub>1</sub>—C<sub>4</sub>-Alkyl steht, oder worinR<sup>1</sup> und R<sup>2</sup> zusammen Alkylen mit 3 bis 6 Kohlenstoffatomen bedeuten,R<sup>3</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet,R<sup>4</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet,

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R<sup>5</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet,R<sup>6</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet und

R<sup>7</sup> und R<sup>8</sup> unabhängig (1) Wasserstoff; (2) Halogen; (3) C<sub>1</sub>—C<sub>4</sub>-Alkyl; (4) C<sub>1</sub>—C<sub>4</sub>-Alkoxy; (5) OCF<sub>3</sub>; (6) Cyano; (7) Nitro; (8) C<sub>1</sub>—C<sub>4</sub>-Haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>—, worin n eine ganze Zahl von 0, 1 oder 2 ist und R<sup>b</sup> für (a) C<sub>1</sub>—C<sub>4</sub>-Alkyl; (b) C<sub>1</sub>—C<sub>4</sub>-Alkyl, substituiert mit Halogen oder Cyano; (c) Phenyl; oder (d) Benzoyl steht; (10) —NR<sup>c</sup>R<sup>d</sup>, worin R<sup>c</sup> und R<sup>d</sup> unabhängig für Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl stehen; (11) R<sup>c</sup>C(O)—, worin R<sup>c</sup> für C<sub>1</sub>—C<sub>4</sub>-Alkyl oder C<sub>1</sub>—C<sub>4</sub>-Alkoxy steht; oder (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup>, worin R<sup>c</sup> und R<sup>d</sup> die gegebenen Definitionen besitzen, bedeuten, mit der Maßgabe, daß R<sup>7</sup> nicht an die 6-Stellung gebunden ist.

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2. Verbindungen nach Anspruch 1, dadurch gekennzeichnet, daß R Methyl; R<sup>1</sup> Wasserstoff oder Methyl; R<sup>2</sup> Wasserstoff oder Methyl; R<sup>3</sup> Wasserstoff oder Methyl; R<sup>4</sup> Wasserstoff oder Methyl; R<sup>5</sup> Wasserstoff oder Methyl; R<sup>6</sup> Wasserstoff oder Methyl bedeuten und R<sup>7</sup> und R<sup>8</sup> unabhängig (1) Wasserstoff; (2) Halogen; (3) C<sub>1</sub>—C<sub>4</sub>-Alkyl; (4) C<sub>1</sub>—C<sub>4</sub>-Alkoxy; (5) OCF<sub>3</sub>; (6) Cyano; (7) Nitro; (8) C<sub>1</sub>—C<sub>4</sub>-Haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>—, worin n eine ganze Zahl von 0, 1 oder 2 steht und R<sup>b</sup> für (a) C<sub>1</sub>—C<sub>4</sub>-Alkyl; (b) C<sub>1</sub>—C<sub>4</sub>-Alkyl, substituiert mit Halogen oder Cyano; (c) Phenyl; oder (d) Benzoyl steht; (10) —NR<sup>c</sup>R<sup>d</sup>, worin R<sup>c</sup> und R<sup>d</sup> unabhängig für Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl stehen; (11) R<sup>c</sup>C(O)—, worin R<sup>c</sup> für C<sub>1</sub>—C<sub>4</sub>-Alkyl oder C<sub>1</sub>—C<sub>4</sub>-Alkoxy steht; oder (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup>, worin R<sup>c</sup> und R<sup>d</sup> die gegebenen Definitionen besitzen, bedeuten.

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3. Verbindungen nach Anspruch 2, dadurch gekennzeichnet, daß R<sup>7</sup> und R<sup>8</sup> unabhängig Wasserstoff; Chlor; Fluor; Brom; Methyl; Methoxy; OCF<sub>3</sub>; Cyano; Nitro; Trifluoromethyl; R<sup>b</sup>SO<sub>n</sub>—, worin n für eine ganze Zahl 2 steht und R<sup>b</sup> für Methyl, Chlormethyl, Trifluormethyl, Cyanomethyl, Ethyl oder n-Propyl steht; —NR<sup>c</sup>R<sup>d</sup>, worin R<sup>c</sup> und R<sup>d</sup> unabhängig für Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl stehen; R<sup>c</sup>C(O)—, worin R<sup>c</sup> für C<sub>1</sub>—C<sub>4</sub>-Alkyl oder C<sub>1</sub>—C<sub>4</sub>-Alkoxy steht; oder SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup>, worin R<sup>c</sup> und R<sup>d</sup> die gegebenen Definitionen besitzen, bedeuten und R<sup>7</sup> in 3-Stellung vorhanden ist.

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4. Verbindungen nach Anspruch 2, dadurch gekennzeichnet, daß R<sup>7</sup> Wasserstoff und R<sup>8</sup> Wasserstoff, Chlor, Brom, Fluor, CF<sub>3</sub> oder R<sup>b</sup>SO<sub>2</sub>—, worin R<sup>b</sup> für C<sub>1</sub>—C<sub>4</sub>-Alkyl steht, bedeuten.

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5. Verbindung nach Anspruch 2, dadurch gekennzeichnet, daß R Methyl; R<sup>1</sup> Methyl; R<sup>2</sup> Methyl; R<sup>3</sup> Wasserstoff; R<sup>4</sup> Wasserstoff; R<sup>5</sup> Wasserstoff; R<sup>6</sup> Wasserstoff; R<sup>7</sup> Wasserstoff und R<sup>8</sup> Wasserstoff bedeuten.

6. Verbindungen nach Anspruch 2, dadurch gekennzeichnet, daß R Methyl; R<sup>1</sup> Methyl; R<sup>2</sup> Methyl; R<sup>3</sup> Wasserstoff; R<sup>4</sup> Wasserstoff; R<sup>5</sup> Methyl; R<sup>6</sup> Wasserstoff; R<sup>7</sup> Wasserstoff und R<sup>8</sup> Wasserstoff bedeuten.

7. Verbindungen nach Anspruch 2, dadurch gekennzeichnet, daß R Methyl; R<sup>1</sup> Wasserstoff; R<sup>2</sup> Wasserstoff; R<sup>3</sup> Wasserstoff; R<sup>4</sup> Wasserstoff; R<sup>5</sup> Wasserstoff; R<sup>6</sup> Wasserstoff; R<sup>7</sup> 3-Chlor und R<sup>8</sup> Chlor bedeuten.

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8. Verbindungen nach Anspruch 2, dadurch gekennzeichnet, daß R Methyl; R<sup>1</sup> Wasserstoff; R<sup>2</sup> Wasserstoff; R<sup>3</sup> Wasserstoff; R<sup>4</sup> Wasserstoff; R<sup>5</sup> Wasserstoff; R<sup>6</sup> Wasserstoff; R<sup>7</sup> Wasserstoff und R<sup>8</sup> Trifluoromethyl bedeuten.

9. Verbindungen nach Anspruch 2, dadurch gekennzeichnet, daß R Methyl; R<sup>1</sup> Methyl; R<sup>2</sup> Methyl; R<sup>3</sup> Wasserstoff; R<sup>4</sup> Wasserstoff; R<sup>5</sup> Wasserstoff; R<sup>6</sup> Wasserstoff; R<sup>7</sup> Wasserstoff und R<sup>8</sup> Trifluoromethyl bedeuten.

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10. Verfahren zur Kontrolle unerwünschter Vegetation, dadurch gekennzeichnet, daß man auf die Fläche, wo eine Kontrolle erfolgen soll, eine herbizid wirksame Menge einer Verbindung nach einem der Ansprüche 1 bis 9 anwendet.

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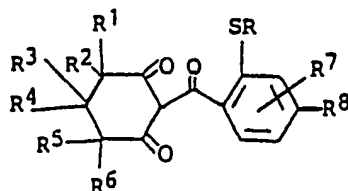
11. Herbizide Zubereitung, dadurch gekennzeichnet, daß sie ein herbizid aktives 2-(2-C<sub>1</sub>—C<sub>4</sub>-Alkylthio-,

**EP 0 186 119 B1**

C<sub>1</sub>—C<sub>4</sub>-Alkylsulfinyl- oder C<sub>1</sub>—C<sub>4</sub>-Alkylsulfonyl-benzoyl)-1,3-cyclohexandion und einen inerten Träger dafür enthält.

12. Herbizide Zubereitung nach Anspruch 11, dadurch gekennzeichnet, daß das 2-(2-C<sub>1</sub>—C<sub>4</sub>-Alkylthio-, C<sub>1</sub>—C<sub>4</sub>-Alkylsulfinyl- oder C<sub>1</sub>—C<sub>4</sub>-Alkylsulfonyl-benzoyl)-1,3-cyclohexandion eine Verbindung nach einem der Ansprüche 1 bis 9 ist.

13. Verfahren zur Herstellung einer Verbindung der Formel

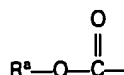


worin

R C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet,

R C<sub>1</sub>—C<sub>4</sub>-Alkyl gegebenenfalls substituiert mit Halogen, bedeutet,

R<sup>1</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet, R<sup>2</sup> Wasserstoff, C<sub>1</sub>—C<sub>4</sub>-Alkyl oder



bedeutet, worin R<sup>a</sup> für C<sub>1</sub>—C<sub>4</sub>-Alkyl steht, oder worin

R<sup>1</sup> und R<sup>2</sup> zusammen Alkylen mit 3 bis 6 Kohlenstoffatomen bedeuten,

R<sup>3</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet,

R<sup>4</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet,

R<sup>5</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet,

R<sup>6</sup> Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl bedeutet und

R<sup>7</sup> und R<sup>8</sup> unabhängig (1) Wasserstoff; (2) Halogen; (3) C<sub>1</sub>—C<sub>4</sub>-Alkyl; (4) C<sub>1</sub>—C<sub>4</sub>-Alkoxy; (5) OCF<sub>3</sub>; (6)

Cyano; (7) Nitro; (8) C<sub>1</sub>—C<sub>4</sub>-Haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>—, worin n eine ganze Zahl von 0, 1 oder 2 ist und R<sup>b</sup> für (a)

C<sub>1</sub>—C<sub>4</sub>-Alkyl; (b) C<sub>1</sub>—C<sub>4</sub>-Alkyl, substituiert mit Halogen oder Cyano; (c) Phenyl; oder (d) Benzoyl steht; (10)

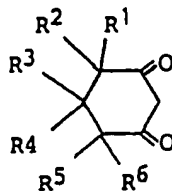
—NR<sup>c</sup>R<sup>d</sup>, worin R<sup>c</sup> und R<sup>d</sup> unabhängig für Wasserstoff oder C<sub>1</sub>—C<sub>4</sub>-Alkyl stehen; (11) R<sup>e</sup>C(O)—, worin R<sup>e</sup> für

C<sub>1</sub>—C<sub>4</sub>-Alkyl oder C<sub>1</sub>—C<sub>4</sub>-Alkoxy steht; oder (12) SO<sub>2</sub>NR<sup>e</sup>R<sup>d</sup>, worin R<sup>e</sup> und R<sup>d</sup> die gegebenen Definitionen

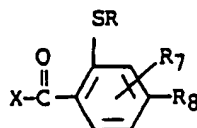
besitzen, bedeuten, mit der Maßgabe, daß R<sup>7</sup> nicht an die 6-Stellung gebunden ist, dadurch

gekennzeichnet, daß man

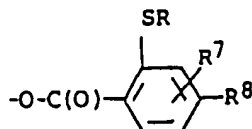
(a) ein Dion der Formel



worin R<sup>1</sup> bis R<sup>6</sup> die gegebenen Definitionen besitzen, mit einem substituierten Benzoyl-Reaktions- teilnehmer der Formel

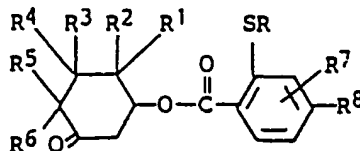


worin R, R<sup>7</sup> und R<sup>8</sup> die gegebenen Definitionen besitzen und X Halogen, C<sub>1</sub>—C<sub>4</sub>-Alkyl-C(O)—O—, C<sub>1</sub>—C<sub>4</sub>- Alkoxy-C(O)—O— oder

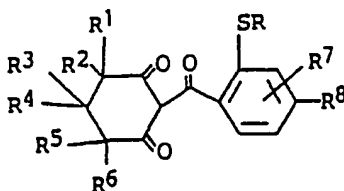


**EP 0 186 119 B1**

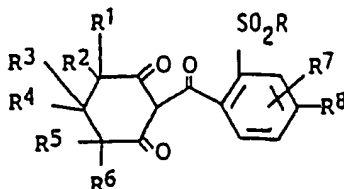
bedeutet, worin R, R<sup>7</sup> und R<sup>8</sup> in diesem Teil des Moleküls identisch sind mit jenen in dem oben gezeigten Reaktionsteilnehmer, mit mindestens einem mol einer milden Base unter Bildung eines Enolesters der Formel



umsetzt, worin R bis R<sup>8</sup> die gegebenen Definitionen besitzen, und man bei der Stufe (2) ein mol des Enolester-Zwischenprodukts mit 1 bis 4 mol einer milden Base und mit 0,01 mol bis etwa 0,5 mol oder mehr einer cyanidquelle unter Bildung einer 2-C<sub>1</sub>—C<sub>4</sub>-Alkylthiobenzoylverbindung der Formel



umsetzt, worin R<sup>1</sup> bis R<sup>8</sup> die oben gegebenen Definitionen besitzen, und gegebenenfalls die 2-C<sub>1</sub>—C<sub>4</sub>-Alkylthiobenzoylverbindung mit einem mol oder zwei mol eines Oxidationsmittels unter Bildung einer Verbindung der Formel



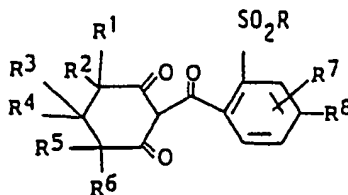
oxidiert, worin R bis R<sup>8</sup> die gegebenen Definitionen besitzen.

14. Verbindungen nach Anspruch 13, dadurch gekennzeichnet, daß X Halogen bedeutet, die milde Base Tri-C<sub>1</sub>—C<sub>6</sub>-alkylamin, Pyridin, eine Alkalimetallcarbonat oder Alkalimetallphosphat ist und die Cyanidquelle ein Alkalimetallcyanid, Cyanohydrine von Methyl-C<sub>1</sub>—C<sub>4</sub>-alkylketonen, Cyanohydrine von Benzaldehyd oder C<sub>2</sub>—C<sub>6</sub>-aliphatischen Aldehyden, Cyanohydrine, Zinkcyanid, Tri-(niedrigalkyl)-silylcyanide oder Cyanwasserstoff ist.

15. Verfahren nach Anspruch 14, dadurch gekennzeichnet, daß X Chlor bedeutet, die milde Base Tri-C<sub>1</sub>—C<sub>6</sub>-alkylamin, Pyridin, Natriumcarbonat oder Natriumphosphat ist und die Cyanidquelle Kaliumcyanid, Acetoncyanohydrin oder Cyanwasserstoff ist.

**Revendications**

1. Un dérivé de formule:



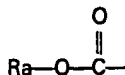
dans laquelle:

R représente un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

R<sup>1</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

R<sup>2</sup> représente un atome d'hydrogène, un radical alkyle en C<sub>1</sub> à C<sub>4</sub>; ou

## EP 0 186 119 B1



5 dans lequel:

Ra est un radical alkyle en C<sub>1</sub> à C<sub>4</sub>; ou

R<sup>1</sup> et R<sup>2</sup> forment ensemble un radical alkylène renfermant de 3 à 6 atomes de carbone;

R<sup>3</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

R<sup>4</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

10 R<sup>5</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

R<sup>6</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>; et

R<sup>7</sup> et R<sup>8</sup> représentent chacun, indépendamment;

(1) un atome d'hydrogène,

(2) un atome d'halogène,

15 (3) un radical alkyle en C<sub>1</sub> à C<sub>4</sub>,

(4) un radical alkoxy en C<sub>1</sub> à C<sub>4</sub>,

(5) OCF<sub>3</sub>,

(6) cyano;

(7) nitro;

20 (8) haloalkyle en C<sub>1</sub> à C<sub>4</sub>;

(9) R<sup>b</sup>SO<sub>n</sub>— dans lequel;

n est égal à 0, 1 ou 2; et

R<sup>b</sup> représente:

(a) un radical alkyle en C<sub>1</sub> à C<sub>4</sub>,

25 (b) un radical alkyle en C<sub>1</sub> à C<sub>4</sub> substitué par un atome d'halogène ou un groupe cyano;

(c) phényle- ou

(d) benzyle;

(10) —NR<sup>c</sup>R<sup>d</sup> dans lequel: R<sup>c</sup> et R<sup>d</sup> représentent indépendamment un atome d'hydrogène ou un radical

alkyle en C<sub>1</sub> à C<sub>4</sub>;

30 (11) R<sup>c</sup>C(O) dans lequel R<sup>c</sup> représente un radical alkyle en C<sub>1</sub> à C<sub>4</sub> ou alkoxy en C<sub>1</sub> à C<sub>4</sub>; ou

(12) —SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> sont tels que définis sous réserve que R<sup>7</sup> ne soit pas attaché en position-6.

2. Les dérivés selon la revendication 1, dans lequel:

R<sup>1</sup> un atome d'hydrogène ou le radical méthyle;

35 R<sup>2</sup> représente un atome d'hydrogène ou le radical méthyle;

R<sup>3</sup> représente un atome d'hydrogène ou le radical méthyle;

R<sup>4</sup> représente un atome d'hydrogène ou le radical méthyle;

R<sup>5</sup> représente un atome d'hydrogène ou le radical méthyle;

R<sup>6</sup> représente un atome d'hydrogène ou le radical méthyle;

40 R<sup>7</sup> et R<sup>8</sup> représentent chacun, indépendamment;

(1) un atome d'hydrogène,

(2) un atome d'halogène,

(3) un radical alkyle en C<sub>1</sub> à C<sub>4</sub>,

(4) un radical alkoxy en C<sub>1</sub> à C<sub>4</sub>,

45 (5) OCF<sub>3</sub>,

(6) cyano;

(7) nitro;

(8) haloalkyle en C<sub>1</sub> à C<sub>4</sub>;

(9) R<sup>b</sup>SO<sub>n</sub>— dans lequel;

50 n est égal à 0, 1 ou 2; et

R<sup>b</sup> représente:

(a) un radical alkyle en C<sub>1</sub> à C<sub>4</sub>,

(b) un radical alkyle en C<sub>1</sub> à C<sub>4</sub> substitué par un atome d'halogène ou un groupe cyano;

(c) le radical phényle- ou

55 (d) benzyle;

(10) —NR<sup>c</sup>R<sup>d</sup> dans lequel: R<sup>c</sup> et R<sup>d</sup> représentent indépendamment un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

(11) R<sup>c</sup>C(O) dans lequel R<sup>c</sup> représente un radical alkyle en C<sub>1</sub> à C<sub>4</sub> ou alkoxy en C<sub>1</sub> à C<sub>4</sub>; ou

(12) —SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> sont tels que définis ci-dessus.

60 3. Le dérivé selon la revendication 2, dans lequel R<sup>7</sup> et R<sup>8</sup> représentent chacun indépendamment un atome d'hydrogène, de chlore, fluor, brome, le radical méthyle, méthoxy, OCF<sub>3</sub>, cyano, nitro, trifluorométhyle, R<sup>b</sup>SO<sub>n</sub> dans lequel n est égal à 2 et R<sup>b</sup> représente les radicaux méthyle, chlorométhyle, trifluorométhyle, cyanométhyle, éthyle ou n-propyle, —NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> représentent chacun, indépendamment, un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>; R<sup>c</sup>C(O) dans lequel R<sup>c</sup> représente

65 un radical alkyle en C<sub>1</sub> à C<sub>4</sub> ou alkoxy en C<sub>1</sub> à C<sub>4</sub> ou SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> et R<sup>d</sup> sont tels que définis ci-

**EP 0 186 119 B1**

dessus et R<sup>7</sup> se trouve en position 3.

4. Les dérivés selon la revendication 2 dans lesquels R<sup>7</sup> représente un atome d'hydrogène et R<sup>8</sup> représente un atome d'hydrogène de chlore, de brome ou de fluor, un groupe CF<sub>3</sub> ou R<sup>b</sup>SO<sub>2</sub> dans lequel R<sup>b</sup> représente un radical alkyle en C<sub>1</sub> à C<sub>4</sub>.

5. Le dérivé selon la revendication 2, dans lequel R représente le radical méthyle, R<sup>1</sup> représente le radical méthyle, R<sup>2</sup> représente le radical méthyle; R<sup>3</sup> représente un atome d'hydrogène; R<sup>4</sup> représente un atome d'hydrogène; R<sup>5</sup> représente un atome d'hydrogène; R<sup>6</sup> représente un atome d'hydrogène; R<sup>7</sup> représente un atome d'hydrogène; et R<sup>8</sup> représente un atome d'hydrogène.

6. Le dérivé selon la revendication 2, dans lequel R représente le radical méthyle, R<sup>1</sup> représente le radical méthyle, R<sup>2</sup> représente le radical méthyle; R<sup>3</sup> représente un atome d'hydrogène; R<sup>4</sup> représente un atome d'hydrogène; R<sup>5</sup> représente le radical méthyle; R<sup>6</sup> représente un atome d'hydrogène; R<sup>7</sup> représente un atome d'hydrogène; et R<sup>8</sup> représente un atome d'hydrogène.

7. Le dérivé selon la revendication 2, dans lequel R représente le radical méthyle, R<sup>1</sup> représente un atome d'hydrogène; R<sup>2</sup> représente un atome d'hydrogène; R<sup>3</sup> représente un atome d'hydrogène; R<sup>4</sup> représente un atome d'hydrogène; R<sup>5</sup> représente un atome d'hydrogène; R<sup>6</sup> représente un atome d'hydrogène; R<sup>7</sup> représente un atome de chlore en position-3 et R<sup>8</sup> représente le chlore.

8. Le composé selon la revendication 2 dans lequel R représente un radical méthyle; R<sup>1</sup> représente un atome d'hydrogène; R<sup>2</sup> représente un atome d'hydrogène; R<sup>3</sup> représente un atome d'hydrogène; R<sup>4</sup> représente un atome d'hydrogène; R<sup>5</sup> représente un atome d'hydrogène; R<sup>6</sup> représente un atome d'hydrogène; R<sup>7</sup> représente un atome d'hydrogène; et R<sup>8</sup> représente un trifluorométhyle.

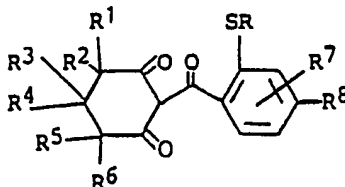
9. Le composé selon la revendication 2 dans lequel R représente un radical méthyle; R<sup>1</sup> représente un radical méthyle; R<sup>2</sup> représente un atome d'hydrogène; R<sup>3</sup> représente un atome d'hydrogène; R<sup>4</sup> représente un atome d'hydrogène; R<sup>5</sup> représente un atome d'hydrogène; R<sup>6</sup> représente un atome d'hydrogène; R<sup>7</sup> représente un atome d'hydrogène; et R<sup>8</sup> représente un trifluorométhyle.

10. Procédé de contrôle d'une végétation indésirable consistant à appliquer à la zone que l'on souhaite contrôler une quantité efficace en tant qu'herbicide d'un dérivé selon les revendications 1 à 9.

11. Une composition herbicide comprenant un 2-(2-C<sub>1</sub>-C<sub>4</sub>-alkylthio, C<sub>1</sub>-C<sub>4</sub>-alkylsulfinyle ou C<sub>1</sub>-C<sub>4</sub>-alkylsulfonylbenzoyl)-1,3-cyclohexanedione efficace en tant qu'herbicide et un support inerte de celle-ci.

12. La composition herbicide selon la revendication 11, 2-(2-C<sub>1</sub>-C<sub>4</sub>-alkylthio, C<sub>1</sub>-C<sub>4</sub>-alkylsulfinyle ou C<sub>1</sub>-C<sub>4</sub>-alkylsulfonylbenzoyl)-1,3-cyclohexanedione est un dérivé selon les revendications 1 à 9.

13. Un procédé de préparation d'un dérivé de formule

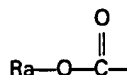


dans laquelle:

R représente un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

R<sup>1</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

R<sup>2</sup> représente un atome d'hydrogène, un radical alkyle en C<sub>1</sub> à C<sub>4</sub>; ou



dans lequel:

R est un radical alkyle en C<sub>1</sub> à C<sub>4</sub>; ou

R<sup>1</sup> et R<sup>2</sup> forment ensemble un radical alkylène renfermant de 3 à 6 atomes de carbone;

R<sup>3</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

R<sup>4</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

R<sup>5</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

R<sup>6</sup> représente un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>; et

R<sup>7</sup> et R<sup>8</sup> représentent chacun, indépendamment;

(1) un atome d'hydrogène,

(2) un atome d'halogène,

(3) un radical alkyle en C<sub>1</sub> à C<sub>4</sub>,

(4) un radical alkoxy en C<sub>1</sub> à C<sub>4</sub>,

(5) OCF<sub>3</sub>,

(6) cyano;

(7) nitro;

(8) haloalkyle en C<sub>1</sub> à C<sub>4</sub>;

(9) R<sup>b</sup>SO<sub>n</sub>— dans lequel;

**EP 0 186 119 B1**

n est égal à 0, 1 ou 2; et

R<sup>b</sup> représente:

(a) un radical alkyle en C<sub>1</sub> à C<sub>4</sub>,

(b) un radical alkyle en C<sub>1</sub> à C<sub>4</sub> substitué par un atome d'halogène ou un groupe cyano;

(c) phényle; ou

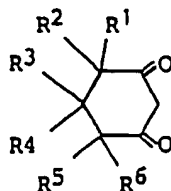
(d) benzyle;

(10) —NR<sup>c</sup>R<sup>d</sup> dans lequel: R<sup>c</sup> et R<sup>d</sup> représentent indépendamment un atome d'hydrogène ou un radical alkyle en C<sub>1</sub> à C<sub>4</sub>;

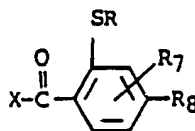
(11) R<sup>e</sup>C(O) dans lequel R<sup>e</sup> représente un radical alkyle en C<sub>1</sub> à C<sub>4</sub> ou alkoxy en C<sub>1</sub> à C<sub>4</sub>; ou

(12) —SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> dans lequel R<sup>c</sup> sont tels que définis sous réserve que R<sup>7</sup> ne soit pas attaché en position-6 consistant:

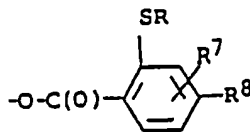
(a) à faire réagir une diène de formule:



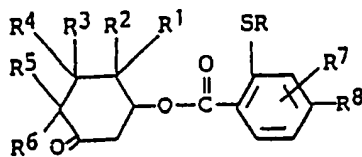
dans laquelle R<sup>1</sup> à R<sup>6</sup> sont tels que définis ci-dessus avec un réactif benzoylé substitué de formule:



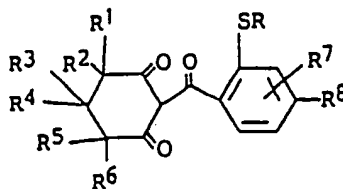
dans laquelle R, R<sup>7</sup> et R<sup>8</sup> sont tels que définis ci-dessus et X représente un atome d'hydrogène, un radical alkyle en C<sub>1</sub>—C<sub>4</sub>—C(O)—O—, C<sub>1</sub>—C<sub>4</sub>—alkoxy—C(O)—O—, ou



dans laquelle R, R<sup>7</sup> et R<sup>8</sup> de cette partie de la molécule sont identiques aux substituants du réactif indiqué ci-dessus avec au moins une mole d'une base modérée pour former un ester énolique de formule:



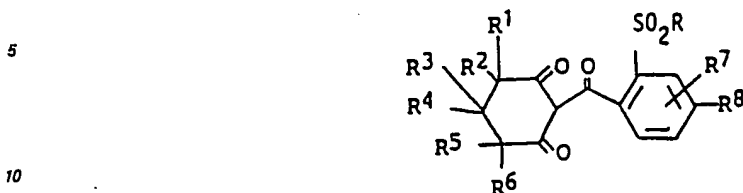
dans laquelle R à R<sup>8</sup> sont tels que définis ci-dessus et dans l'étape (2), on fait réagir une mole de l'ester énolique intermédiaire avec 1 à 4 moles d'une base modérée et de 0,01 mole à environ 0,5 mole ou plus d'une source de cyanure pour former un dérivé 2-C<sub>1</sub>—C<sub>4</sub>-alkylthiobenzoyl de formule:



dans laquelle R<sup>1</sup> à R<sup>8</sup> sont tels que définis ci-dessus et éventuellement on oxyde le dérivé 2-C<sub>1</sub>—C<sub>4</sub>-alkyl-

**EP 0 186 119 B1**

thiobenzoyl à l'aide de 1 ou 2 moles d'un agent d'oxydation pour former un dérivé de formule:



dans laquelle R à R<sup>8</sup> sont tels que définis ci-dessus.

14. Le procédé selon la revendication 13, dans lequel X représente un atome d'hydrogène, la base modérée est la tri-C<sub>1</sub>—C<sub>4</sub>-alkylamine, pyridine, un carbonate de métal alcalin ou un phosphate de métal alcalin et la source de cyanure est un cyanure de métal alcalin, des cyanohydrines de méthyl-C<sub>1</sub>—C<sub>4</sub>-alkyl-cétones, des cyanohydrines de benzaldéhydes ou des cyanohydrines d'aldéhydes aliphatiques en C<sub>2</sub> à C<sub>5</sub>, du cyanure de zinc; cyanures de tri(alkyl-inférieure)-silyles ou acide cyanhydrique.

15. Le procédé de la revendication 14 dans lequel X représente un atome de chlore, la base modérée est la tri-C<sub>1</sub>—C<sub>4</sub>-alkylamine, le pyridine, le carbonate de sodium ou le phosphate de sodium et la source de cyanure, le cyanure de potassium, l'acétone cyanohydrine ou l'acide cyanhydrique.